

UNCLASSIFIED

AD NUMBER

AD869601

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors;
Administrative/Operational Use; FEB 1970. Other requests shall be referred to Office of Naval Research, Arlington, VA 20360.

AUTHORITY

ONR ltr 27 Jul 1971

THIS PAGE IS UNCLASSIFIED

HPC 70-111



AD 869601

**MONSANTO/WASHINGTON UNIVERSITY
ONR/ARPA ASSOCIATION**

THE EFFECT OF THERMAL TREATMENT ON THE INTERFACE STRENGTH
IN GRAPHITE/POLYCARBONATE COMPOSITES

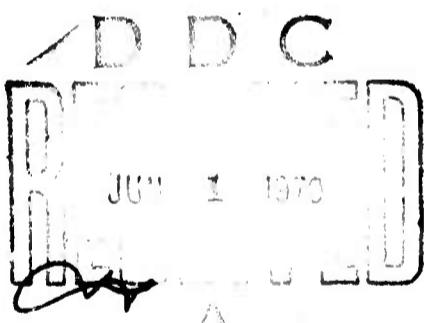
BY

F. S. CHENG, J. L. KARDOS AND T. L. TOLBERT

FILE COPY

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Director of Material Sciences, Office of Naval Research.

Wash. C. 22360



PROGRAM MANAGER
ROLF BUCHDAHL

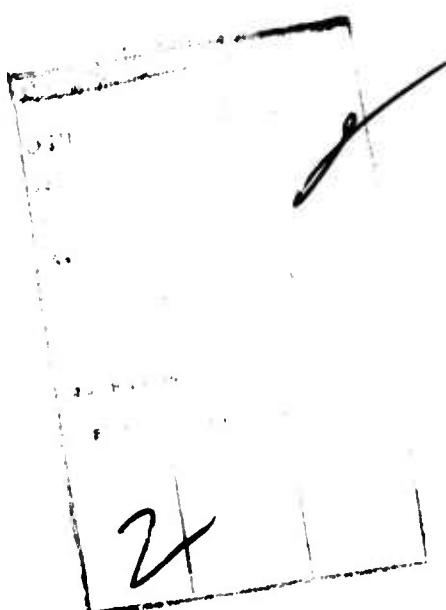
MONSANTO RESEARCH CORPORATION
A SUBSIDIARY OF MONSANTO COMPANY

800 N. LINDBERGH BOULEVARD

ST. LOUIS, MISSOURI 63166



20



NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

DDC release to CFSTI is not authorized.

HPC 70-111

MONSANTO/WASHINGTON UNIVERSITY
ONR/ARPA ASSOCIATION

THE EFFECT OF THERMAL TREATMENT ON THE INTERFACE STRENGTH
IN GRAPHITE/POLYCARBONATE COMPOSITES

F. S. Cheng, J. L. Kardos and T. L. Tolbert

February 1970

Program Manager
Rolf Buchdahl

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Director of Material Sciences, Office of Naval Research.

Monsanto Research Corporation
800 North Lindbergh Blvd.
St. Louis, Missouri 63166

FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0214 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl (phone 314-694-4721). The contract is funded for \$6,000,000 and expires 30 April 1971.

THE EFFECT OF THERMAL TREATMENT ON THE INTERFACE STRENGTH IN GRAPHITE/POLYCARBONATE COMPOSITES

F. S. Cheng, J. L. Kardos and T. L. Tolbert*
Materials Research Laboratory and
Department of Chemical Engineering
Washington University
St. Louis, Missouri 63130

Abstract

Pronounced effects of thermal treatment on the properties of graphite/polycarbonate composites have been demonstrated and studied. At a 20 percent volume loading of random-in-a-plane, discontinuous fibers, both specimen strength and modulus were found to be very sensitive to initial molding temperature and to subsequent heat treatments. Scanning electron micrographs of tensile fracture surfaces show that the matrix adheres to the fibers more tenaciously and in greater quantities as the tensile strength increases. Preliminary diffraction evidence indicates that the polycarbonate has epitaxially crystallized on and around the graphite fibers in the case of the annealed samples. The increases in composite strength are attributed to increases in interface strength which arise from better wetting and partial crystallization at the interface.

*Affiliate Professor of Materials Science, from Monsanto Company, St. Louis, Missouri.

THE EFFECT OF THERMAL TREATMENT ON THE INTERFACE STRENGTH IN GRAPHITE/POLYCARBONATE COMPOSITES

F. S. Cheng, J. L. Kardos and T. L. Tolbert*

Department of Chemical Engineering
and Materials Research Laboratory
Washington University
St. Louis, Missouri 63130

Introduction

Over the past few years graphite fibers have been developed to a point that they now can compete with, and in some aspects surpass, glass fibers as reinforcing agents. In addition to replacing glass in thermosetting systems such as filament wound epoxy composites, graphite fibers are beginning to be employed as a discontinuous reinforcement for thermoplastics [1]. This is a particularly advantageous combination in that the very high specific properties normally achieved only with reinforced thermosets can be obtained in these systems without the usual sacrifice in processability.

The level of crystallinity in a number of so-called high temperature thermoplastics, such as polycarbonate and polysulfone, is quite low under most circumstances. However, under certain conditions these materials can be made to crystallize and thereby to change markedly in bulk properties. For example, the stiffness of polycarbonate resin can be increased 50 percent or more by simply holding it at a temperature above which melting occurs; increases of 10 degrees in heat deflection temperature are not uncommon under these conditions. Crystallinity also can be promoted by exposure to certain solvent environments [2, 3] or by introducing nucleating sites in the form of a filler or substrate [4].

*Affiliate Professor of Materials Science, from Monsanto Company, St. Louis, Missouri.

Graphite fibers present a relatively high-energy surface which should be ideal for nucleating or "promoting" crystallization in such systems; in fact, graphite has been reported to contribute to epitaxial crystallization of hexamethylene-diammonium adipate [5] and polyethylene [6].

This raises the possibility that one might be able to tailor the interface in a graphite/thermoplastic composite and improve performances of the system by subjecting it to controlled thermal treatment which will cause the matrix to crystallize epitaxially on and around the fiber. The result would be improved fiber/matrix bonding brought about by generation of a transition region of intermediate modulus around the fiber, which should permit more efficient transmission of stresses and therefore higher composite strength. Improvements in composite properties have in fact been achieved this way. We have been able to change the character of the interface and improve the properties of graphite/polycarbonate composites, for example, by simply varying thermal conditions during fabrication. This report summarizes initial results from studies on changes in composite mechanical properties and fracture surface morphology due to such variations.

Experimental

Two types of graphite fibers, Thorne 40 (Union Carbide Corporation, modulus - 36.5×10^6 psi, strength - 203×10^3 psi) sized with polyvinyl alcohol and Hercules HMG (modulus - 56×10^6 psi, strength - 300×10^3 psi) sized with Epon 828, were used in this study. The fibers were cut into 1/8 inch lengths and sonically dispersed in a 75 percent methanol-25 percent water solution along with 60-100 mesh polycarbonate powder (General Electric Lexan 145). A preform mat of two-dimensionally random fibers

uniformly mixed with resin powder was prepared from the suspension by draining off the solution through a filter shaped like the final sample (5" x 1/2" x 1/16" plate) in the bottom of the container. The matt was dried at 110°C for eight hours under vacuum and then compression molded. Molding was carried out at 5000 psi using various temperature cycles. After heating the fiber/resin mixture under pressure to the molding temperature, specimens were (1) held at 190°C for 10 minutes and then slowly cooled to room temperature, (2) held at 275°C for 10 minutes and cooled, or (3) held at 275°C for 10 minutes and then annealed for three hours at 245°C before cooling. A total of 12 specimens were prepared under each regime. An equal number of unfilled bars of the same geometry molded under the same conditions was prepared as standards. Specimens were characterized by dynamic mechanical measurements, tensile stress-strain tests, and scanning electron microscopy (tensile fracture surfaces).

Results and Discussion

Tensile data for both unfilled and Hercules fiber filled specimens are shown in Table I. Note that only relatively minor changes in tensile mechanical properties were observed for the pure matrix specimens regardless of the treatment used. Dramatic changes in the properties of the reinforced specimens were observed, however. At 20 volume percent fiber loading, specimen strength and modulus were found to be very sensitive both to initial molding temperature and to subsequent annealing treatments. For example, the tensile strength of specimens reinforced with Hercules fiber was nearly doubled by changing the thermal history from molding the specimen at 190°C (25°C above T_g) to molding at 275°C and annealing at 245°C. Since the thermal treatment

used here should not effect the fibers themselves and the effect on unfilled resin properties is small, the fibers must have in some way contributed to or promoted changes in the matrix during thermal treatment. Similar, though slightly smaller, effects were observed in the Thornel 40 reinforced system.

Figures 1 to 3 are scanning electron micrographs of exposed Thornel fibers on tensile fracture surfaces of samples molded under three different conditions. For comparison, in Figure 4 we show a micrograph of the surface of a Thornel fiber "as-received." Note the similarity of this fiber to that shown in the micrographs of the composite molded at 190°C; this at least implies that the degree of adhesion in the 190°C composite is quite low. In fact it is clear that, in progressing from the 190°C treatment to molding at 275°C and then to preparation of samples at 275°C and annealing them, changes occur which result in more and more polymer matrix left adhering to the graphite after fracture. The same phenomenon occurs in the Hercules samples. Figure 5 shows the marked increase in adhering polymer from relatively bare fibers resulting from the 190°C treatment to fibers from samples which had been fabricated at 275°C and then annealed at 245°C. Again the implication is that the strength of the fiber/matrix bond is increasing. In each case the increase in the amount of polymer adhering to the fibers after fracture corresponds to increases in both tensile strength and tensile modulus. A similar trend was reported previously for glass-filled polyphenylene oxide [7] and glass filled epoxy systems [8], where the interface strength was varied experimentally with the use of coupling and release agents. It seems likely therefore that increased composite strength in the polycarbonate/graphite fiber system arises directly from increased interface strength and is therefore a function of better wetting and adhesion.

In light of References 5 and 6, it is likely that crystallization phenomena are involved in the mechanism for improved adhesion. There are also several experimental indications that the resin may be epitaxially crystallizing on and near the graphite surfaces. For example, strengthening has been observed to occur only when the fabrication temperature is above the normal melting point of crystalline polycarbonate, in this case about 265°C. Melting of any microcrystalline regions should not only permit better wetting of the fiber surface but also promote redevelopment of crystallinity at favored nucleation sites on the graphite surface [5, 6]. Furthermore, we have obtained limited transmission electron diffraction evidence from detachment replicas of the fibers at the fracture surfaces in the annealed samples, which indicate that oriented polycarbonate is present on the fiber surfaces. Discrete arcs corresponding to polycarbonate unit-cell spacings rapidly disappeared when the very low beam current was increased, even when a cold stage was employed, indicating that the polymer melted in the heat of the beam. High magnification scanning electron micrographs of the fiber surfaces in the annealed samples and those molded at 275°C often reveal polymer particles which appear to have an angular morphology such as can be seen in Figure 6. It is possible, of course, that oriented material could arise from deformation orientation during fracture as well as from crystallization. This seems unlikely, however, especially in light of the fact that the glass transition temperature of the matrix in all of the composites, as determined by non-destructive torsion pendulum measurements, is from 10 to 13°C above that of the unfilled polymer molded under the same conditions (see Table I); again, this indicates a considerable effect of the fiber surface on order developed within the matrix material. At this point we do not know to what extent the sizing material participates in the

strengthening mechanism. Limited results from samples containing size-free fibers indicate that the sizing is not responsible for the large increases observed, although sized fibers do seem to yield slightly stronger composites. A systematic study of the nature of the interface in this system is still underway and more detailed results will be presented in the near future.

Acknowledgment

This research was conducted under the auspices of the Monsanto/Washington University Association sponsored by the Advanced Research Projects Agency, Department of Defense, and the Office of Naval Research under Contract No. N00014-67-C-0218. We wish to thank Mr. J. D. Fairing of the Monsanto Company for providing most of the scanning electron micrographs.

REFERENCES

1. L. W. Toth, "Compression Molding with Advanced Fibers," Fourth Annual Symposium on High-Performance Composites, St. Louis, Missouri, April 8-9, 1969.
2. J. P. Mercier, G. Groeninckx and M. Lesne, "Some Aspects of Vapor-Induced Crystallization of Polycarbonate of Bisphenol A," *J. Pol. Sci., Part C*, No. 16 (1967), p. 2059.
3. B. J. MacNulty, "Microscopic Observations of Unreported Crystalline Formations in Polycarbonate and Polysulfone," *J. Materials Sci.*, Vol. 4 (1969), p. 841.
4. J. A. Koutsky, A. K. Walton and E. Baer, "Heterogeneous Nucleation of Polyethylene Melt on Cleaved Surfaces of Alkali Halides," *Polymer Letters*, Vol. 5 (1967), p. 185.
5. P. D. Frayer and J. B. Lando, "Crystallization and Reaction on Graphite-Like Fiber Surfaces," *J. Colloid and Interface Sci.*, Vol. 31 (1969), p. 145.
6. E. Baer, J. L. Koenig and F. Tuinstra, "Research on Graphite-Fiber Resin-Matrix Composites," Air Force Materials Laboratory Technical Report AFML-TR-66-310, Part IV, Vol. 1 (1969), p. 16.
7. A. Wambach, K. Trachte and A. DiBenedetto, "Fracture Properties of Glass Filled Polyphenylene Oxide Composites," *J. Composite Materials*, Vol. 2 (1968), p. 266.
8. A. S. Kenyon, "Role of the Interface in Glass-Epoxy Composites," *J. Colloid and Interface Sci.*, Vol. 28 (1968), p. 761.

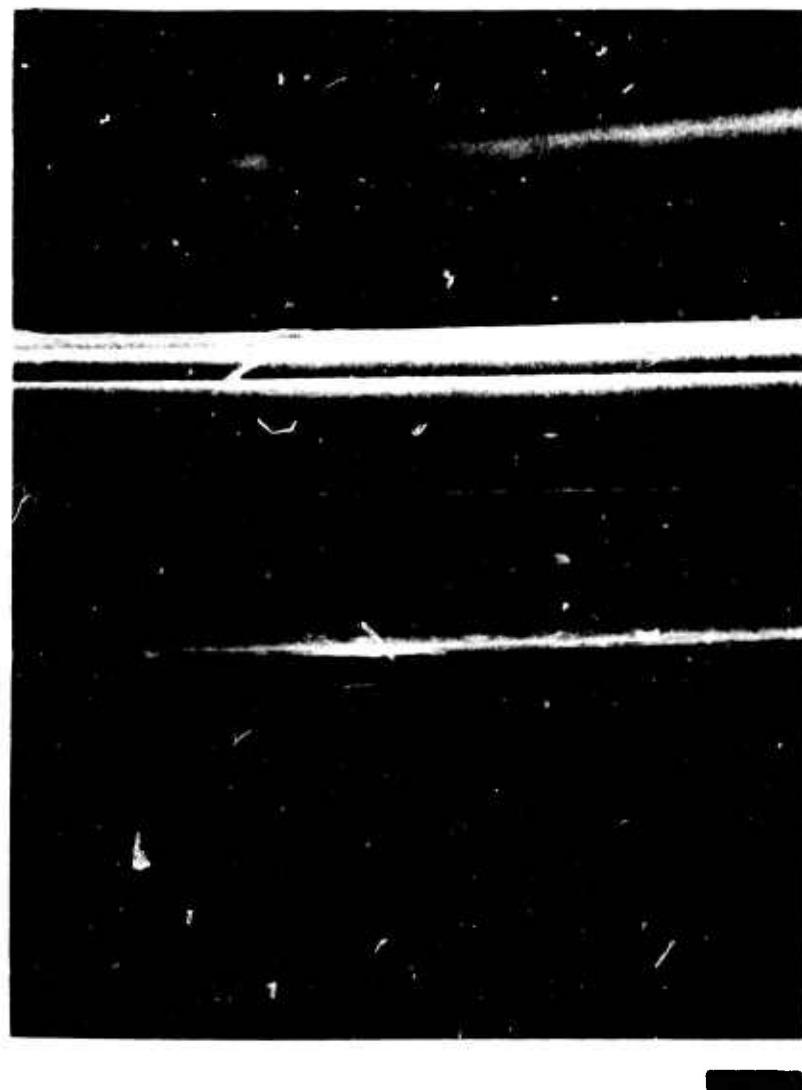


Figure 1. Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 190°C. Note the similarity of this fiber's surface to that of the "as-received" fiber in Figure 4. The scale bar represents 2 microns.



Figure 2. Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 275°C. Note the increase in adhering matrix on the fiber over that seen in Figure 1. The scale bar represents 2 microns.

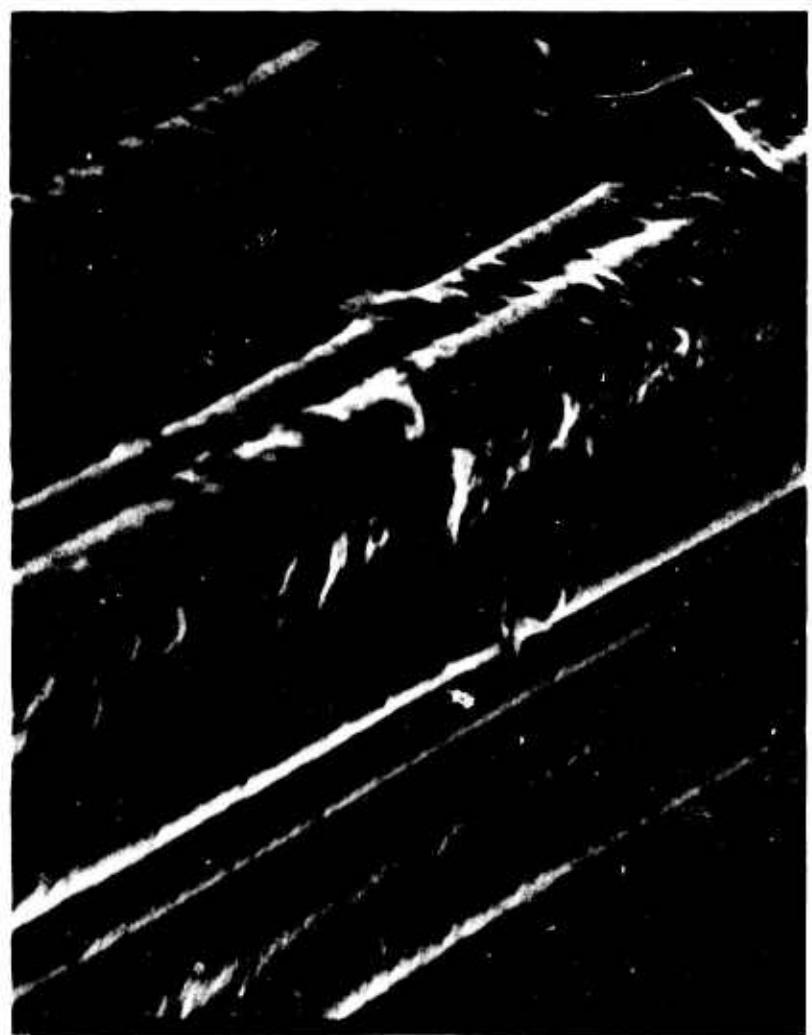


Figure 3. Scanning electron micrograph of exposed Thorne fiber on the tensile fracture surface of a sample molded at 275°C and then annealed at 245°C for three hours. Note the coating of matrix which almost completely covers the fiber. The scale bar represents 2 microns.



Figure 4. Scanning electron micrograph of an "as-received" Thornel fiber. The scale bar represents 2 microns.



A



B

Figure 5. Scanning electron micrographs of exposed Hercules fibers on the tensile fracture surface of samples (A) molded at 190°C and (B) molded at 275°C and then annealed at 245°C for three hours. Note the increase in amount of adhering plastic from (A) to (B). The scale bar represents 2 microns.



Figure 6. High magnification scanning electron micrograph of a Thornel fiber surface in the annealed sample. The adhering polymer particles appear to have an angular morphology characteristic of polymer crystals. The scale bar indicates 1 micron.

TABLE I

EFFECT OF THERMAL TREATMENT ON PROPERTIES OF
DISCONTINUOUS GRAPHITE/POLYCARBONATE COMPOSITES

Property	Thermal Treatment		
	190°C	275°C	275°C Annealed at 245°C
Tensile Strength (x 10 ³) psi			
Unfilled	8.3	8.6	8.2
Filled	8.6	13.7	16.3
% Strain			
Unfilled	5.1	6.2	2.8
Filled	0.79	0.84	0.76
Tensile Modulus (x 10 ⁶) psi			
Unfilled	0.32	0.34	0.57
Filled	1.93	2.90	3.78
Glass Transition Temperature, T _g , °C			
Unfilled	154	155	157-159
Filled	167-169	167-168	168

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION Unclassified
Monsanto Research Corporation	2b. GROUP

3 REPORT TITLE

The Effect of Thermal Treatment on the Interface Strength in Graphite/Polycarbonate Composites

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

5 AUTHOR(S) (First name, middle initial, last name)

F. S. Cheng, J. L. Kardos and T. L. Tolbert

6 REPORT DATE February 1970	7a. TOTAL NO. OF PAGES 25	7b. NO. OF REFS 8
8a. CONTRACT OR GRANT NO. N00014-67-C-0218	9a. ORIGINATOR'S REPORT NUMBER(S) HPC 70-111	
b. PROJECT NO.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.		
d.		

10 DISTRIBUTION STATEMENT

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Director of Material Sciences, Office of Naval Research.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Office of Naval Research Washington, D. C. 20360
-------------------------	-------------------------------------------------------------------------------------------------

13 ABSTRACT

Pronounced effects of thermal treatment on the properties of graphite/polycarbonate composites have been demonstrated and studied. At a 20 percent volume loading of random-in-a-plane, discontinuous fibers, both specimen strength and modulus were found to be very sensitive to initial molding temperature and to subsequent heat treatments. Scanning electron micrographs of tensile fracture surfaces show that the matrix adheres to the fibers more tenaciously and in greater quantities as the tensile strength increases. Preliminary diffraction evidence indicates that the polycarbonate has epitaxially crystallized on and around the graphite fibers in the case of the annealed samples. The increases in composite strength are attributed to increases in interface strength which arise from better wetting and partial crystallization at the interface.

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Graphite/polycarbonate composites						
Interfaces						
Thermal treatment						
Annealing						
Strength						
Stiffness						
Crystallinity						
Scanning electron microscopy						
Glass transition temperature						

DD FORM 1 NOV 55 1473 (BACK)

(PAGE 2)

Security Classification